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Abstract of the Disclosure

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Germicidal agent for use in aqueous systems, which germicidal agent is based on hydrogen peroxide and comprises at least one of the following:

- a p-hydroxybenzoic acid compound selected from the group consisting of p-hydroxybenzoic acid, salts thereof and alkyl esters thereof of from 1 to 4 carbon atoms in the alkyl moiety;

- at least one nitrogen heterocyclic aromatic compound which does not decompose upon reaction with H_2O_2 and which contains at least one hydroxyl group or carboxyl group and which may be in salt or alkyl ester form, wherein the alkyl moiety has of from 1 to 4 carbon atoms;

- an amino sulfonic acid of the formula R_2NSO_3H wherein R is hydrogen or alkyl of from 1 to 6 carbon atoms, or a salt of such amino sulfonic acid, as a synergistic ingredient.

* * *

The invention concerns an H_2O_2-containing germicidal agent for aqueous systems and to the use thereof.

Water, which up to recently has been an inexpensive substance abundantly available in nature, is increasingly becoming a valuable and expensive resource material, especially for industry, and it is not always available in the quantity desired. For some time, therefore, efforts have been made in communities and in industry to limit the consumption of fresh water, and for that purpose to purify and reuse waste water--in other words to recycle it by means of one or more regenerating treatments. Typical of these efforts are cooling water recycling systems in various industries and recirculating systems in swimming pool installations.

For instance, in closed circulating systems used in paper factories, water is separated from waste streams mechanically, e.g., by filtration, and is reused. The waste water that is recycled generally contains high concentrations of impurities which constitute nutrients for microorganisms of all kinds. Precisely in the case of papermills, the cellulose present in the filtered water is a very good nutrient medium for algae, fungi and other microbes whose access can hardly be prevented even in closed waste-water systems. This microbial flora is

manifested by slime which can cause considerable trouble at various points in the circulation system.

It is known to prevent the occurrence of microorganisms in waters of all kinds by the addition of a suitable germicidal agent. It is also known to use for this purpose germicides which act without leaving afterproducts, or at least without leaving in the water substances having undesirable or even toxic or corrosion-promoting properties.

Such a known germicide, which is completely consumed without the formation of any residues, is hydrogen peroxide, which breaks down into oxygen and water. Hydrogen peroxide not only has bactericidal, deodorizing, oxidizing and antiphlogistic actions, but also fungistatic and fungicidal actions (cf., for example, Dermatologische Wochenschrift, 152, p. 1105 [1966]).

Hydrogen peroxide, however, is not universally usable as a germicidal agent, and especially it is not suitable for the continuous treatment of certain waste waters, because there are a number of microorganisms which are capable of forming resistant strains within a relatively short time, which are no longer attacked by hydrogen peroxide.

German Offenlegungsschrift 2,228,011 has disclosed a

biological clarification method in which hydrogen peroxide is added to the waste water, and provides the oxygen required for the entire aerobic bacterial clarification, while at the same time preventing the development of filamentous bacteria. In this case, therefore, use is made of the selective effectiveness of hydrogen peroxide, on the basis of which specific microorganisms are completely destroyed, but at the same time the growth conditions for other microorganisms are optimized.

To render aqueous systems completely germ-free, it has therefore also been proposed to use hydrogen peroxide together with organic compounds as a germicidal agent. For example, German Offenlegungsschrift 2,221,047 describes a method of preparing a purification and sterilization solution for soft contact lenses, in which hydrogen peroxide or water-soluble, nontoxic peroxides are used together with phenyl mercury(II) salts, especially with sodium ethyl mercury thiosalicilate, in the form of an aqueous, isotonic solution. This known agent is not universally usable, either, especially on account of the toxicity of the mercury, which forbids the use of such an agent, not just in bathing establishments and the like, for example, but also in industry, such as the paper industry, for example, when the paper is intended for use in the packaging of foods, or in the pharmaceutical industry or in other areas where, in the event of a rupture in the circulation system, materials intended

for use by man might come in contact with toxic substances.

There is a need, therefore, for another germicidal agent which will have a broader spectrum of action than hydrogen peroxide alone.

The invention is addressed to the problem of satisfying this need and of creating a germicidal agent for aqueous systems on a basis of hydrogen peroxide, which is universally usable, effectively destroys germs of all kinds, does not leave undesirable or corrosion-producing afterproducts, and neither is toxic in itself nor yields any toxic degradation products.

This problem is solved in accordance with the invention by a germicidal agent of the initially mentioned kind having a content of p-hydroxybenzoic acid or of one of its salts or alkyl esters of 1 to 4 carbon atoms and/or at least one nitrogen-heterocyclic, aromatic compound which does not react with hydrogen peroxide with degradation, and which contains at least one hydroxyl group and/or at least one carboxyl group, or salts or alkyl esters thereof of 1 to 4 carbon atoms, and/or an aminosulfonic acid of the general formula R_2NSO_3H, wherein R represents hydrogen or an alkyl group of 1 to 6 carbon atoms, or a salt thereof, as a synergetic active substance or mixture of active substances, as the case may be, and a corrosion inhibitor if desired.

It has been found surprisingly that the germicidal agent of the invention has a synergetic effect, i.e., that the action of the two components, hydrogen peroxide and aromatic compound and/or aminosulfonic acid, combined is substantially greater than the mere additive effectiveness of the components of the same composition. One advantage of the agent of the invention for its practical use consists in the fact that the stability of the hydrogen peroxide is not impaired by the germicidally active additive or germicidally active additives, as the case may be, and thus the shelf life of the germicide and hence the economicalness of its use are not impaired. Another important advantage of the agent of the invention consists in the fact that the substances remaining after water treatment, which are not completely used up by chemical reaction like the hydrogen peroxide itself, have virtually no properties physiologically objectionable for the human organism. This is especially important in the use of the agent of the invention, say, for the disinfection of swimming pool water or, in the industrial area, for use in paper mills in which wrapping material for foods is manufactured.

The p-hydroxybenzoic acid ethyl and propyl esters which can be used as synergetic active substances in addition to hydrogen peroxide are, for example, physiologically entirely unobjectionable and therefore approved under the name, "PHB esters," as food preservatives.

In a preferred embodiment of the agent of the invention the agent contains the synergetic active substance or substances in the form of aqueous and, in some cases, mineral acid solutions. The addition of a small amount of a mineral acid has the advantage that any active substance of comparatively low solubility in water that may be contained in the agent can be easily dissolved therein.

Additional advantageous developments of the agent of the invention consist in incorporating the synergetic active substance or substances in amounts between 0.1 and 5% by weight, in using as an aromatic nitrogen-heterocyclic compound one having only one nitrogen ring atom, and in using as an aromatic nitrogen-heterocyclic compound a hydroxyquinoline and/or a pyridine dicarboxylic acid.

Preferred are those germicidal agents which contain 8-hydroxyquinoline and/or dipicolinic acid as aromatic nitrogen-containing compound.

The germicides of the invention contain hydrogen peroxide preferably in the form of a commercial aqueous, stabilized or unstabilized solution. The common hydrogen peroxide stabilizing agents, such as sodium pyrophosphate for example, impair neither the synergetic effect nor the properties of the individual components contained in the agent of the invention.

The problem described in the beginning is furthermore solved by the use of the germicidal agent of the invention in a concentration corresponding to 0.01 to 2 ml of a 35% aqueous hydrogen peroxide solution per liter of the medium being treated.

A corrosion inhibitor, such as ammonium nitrate for example, can be added, if desired, to the germicidal agent if parts sensitive or liable to corrosion are present in the system, such as fittings, pumps and couplings of any kind, without thereby impairing the synergetic effect between the hydrogen peroxide and the organic compound.

The addition of the agent of the invention to the aqueous medium to be disinfected is performed by means of conventional apparatus, such as continuously or periodically operating proportioning apparatus made of a material compatible with hydrogen peroxide.

EXAMPLES

The invention will be further explained with the aid of the examples and of a description of an experiment.

The Examples 1 to 7 that follow represent effective germicidal agents in accordance with the invention. They are prepared by mixing 35 wt.-% aqueous hydrogen peroxide solution with the stated synergetic active substances in the ratio given in each case, and they can be stored in this form unobjectionably, and without losing any of their effectiveness, and they can be used at any time after their preparation.

Example 1:

35 wt.-% H_2O_2
2 wt.-% ammonium aminosulfonate
Balance, water

Example 2:

35 wt.-% H_2O_2
1.5 g/l p-hydroxybenzoic acid ethyl ester
Balance, water

Example 3:

35 wt.-% H_2O_2
0.5 wt.-% dipicolinic acid
Balance, water

Example 4:

35 wt.-% H_2O_2
2 wt.-% ammonium aminosulfonate
0.5 g/l sodium pyrophosphate
Balance, water

Example 5:

35 wt.-% H_2O_2
2 wt.-% ammonium aminosulfonate
0.25 wt.-% dipicolinic acid
Balance, water

Example 6:

35 wt.-% H_2O_2
2 wt.-% 8-hydroxyquinoline
0.25 wt.-% dipicolinic acid
plus sulfuric acid until the hydroxyquinoline is completely dissolved
Balance, water

Example 7:

35 wt.-% H_2O_2

2 wt.-% 8-hydroxyquinoline

1.5 g/l p-hydroxybenzoic acid ethyl ester

plus sulfuric acid until the hydroxyquinoline is completely dissolved

Balance, water.

The germicidal effectiveness of the agents of the invention in accordance with Examples 1 to 7 was determined by means of the following experiment.

For the concentration of cellulose decomposing agents, 5 g of cellulose powder, 0.1 g of yeast extract and 5 g of humus earth are added to a Dubo's salt solution, consisting of 0.5 g of $NaNO_3$, 1 kg of K_2HPO_4, 0.5 g of $MgSO_4 \cdot 7H_2O$, 0.5 g of KCl, 0.01 g of $FeSO_4 \cdot 7H_2O$ and one liter of distilled water, and the mixture is aired for several weeks. Experimental batches were then prepared which contained Dubo's salt solution and 10% of the concentrated cellulose decomposing agent substrate. 0.25 ml/l and 0.05 ml/l of the germicidal agents of Examples 1 to 7 were added to these experimental batches; the mixtures were incubated at 15°C and slightly aired. At the beginning of the experiments,

as well as one day, seven days, fourteen days and twenty days afterward, the total germ count was determined on PC agar (10 days of incubation at 22°C. In addition, blind tests were peformed, i.e., tests without the addition of a germicidal agent, in order to determine the total germ count originally contained in the experimental mixtures. For the comparison and illustration of the synergetic effect achieved with the agents of the invention, the same experimental mixtures were tested under the same conditions without hydrogen peroxide, i.e., with only the organic components of Examples 1 to 7 (including $Na_2H_2P_2O_7$ and H_2SO_4), and finally, again for purposes of comparison, the germicidal effect of 35 wt.-% hydrogen peroxide solution in commercial form was tested alone, i.e., without the addition of other active substances.

The results are recorded in the following Tables 1 and 2. Given in each case is the number of living germs contained in one milliliter of the experimental mixtures (the expression, $<10^1$, means that no living germs could be found in 0.1 ml of mixture). In the case of Examples 1' to 7', the germicidal agents are the agents which contained no hydrogen peroxide, but otherwise are the same as the agents of Examples 1 to 7.

Table 1

(Germicidal agent concentration: 0.25 ml/l of test mixture)

Germicidal agent	Live Germ Count			
	Initial	1 Day	7 Days	14 Days
--	7×10^4	6×10^5	5×10^6	2×10^6
Example 1	2×10^4	$< 10^1$	$< 10^1$	$< 10^1$
Example 1'	2×10^5	4×10^5	3×10^7	5×10^5
Example 2	2×10^4	$< 10^1$	$< 10^1$	$< 10^1$
Example 2'	2×10^5	2×10^6	3×10^6	10^6
Example 3	2×10^5	$< 10^1$	$< 10^1$	$< 10^1$
Example 3'	2×10^5	2×10^6	5×10^5	10^5
Example 4	5×10^5	$< 10^1$	$< 10^1$	$< 10^1$
Example 4'	2×10^6	3×10^5	4×10^5	5×10^5
35% H_2O_2 (comparison)	5×10^4	2×10^2	5×10^1	5×10^2

Table 2

(Germicidal agent concentration: 0.05 ml/l of test mixture)

Germicidal agent	Live Germ Count			
	Initial	1 Day	7 Days	14 Days
-	3×10^8	3×10^8	8×10^6	10^7
Example 5	3×10^8	2×10^3	$< 10^1$	$< 10^1$
Example 5'	3×10^8	1×10^8	8×10^6	3×10^6
Example 6	3×10^8	6×10^2	$< 10^1$	$< 10^1$
Example 6'	3×10^8	1×10^8	10^6	10^6
Example 7	3×10^8	3×10^2	$< 10^1$	$< 10^1$
Example 7'	3×10^8	1×10^8	3×10^7	2×10^6
35% H_2O_2 (comparison)	3×10^8	10^6	10^3	2×10^4

The results given in Tables 1 and 2 show that, when the germicidal agents of the invention are used in a concentration of 0.25 ml/l, no live germs were to be found after one day in 0.1 ml of the test solutions, whereas with 35 weight-percent solutions of H_2O_2, 2×10^2 were found after one day, and after fourteen days as much as 5×10^2 were found, and, with the additive organic active substances alone, i.e., without the addition of H_2O_2, 3×10^5 to 2×10^6 were found after one day and, after 14 days, 10^5 to 10^6 live germs were found. From this it appears that the effectiveness of the agents of the invention is not, as might have been expected, the mere sum of the effectivenesses of H_2O_2 and the additionally used active agent, but that a genuinely synergetic effect is produced by the agents of the invention. The results furthermore show that neither the presence of a conventional stabilizer for hydrogen peroxide (Example 4) nor the presence of small amounts of a mineral acid (Examples 6 and 7) are able to impair the synergetic effect and the effectiveness of the agents of the invention.

The agents of the invention are thus outstandingly suited quite generally for the sterilization and/or disinfection of aqueous systems, not only for waste waters recirculated in industry, but also in other fields, as for example the treatment of swimming pool water.

It will be understood that the specification and examples are illustrative but not limitative of the present invention and that other embodiments within the spirit and scope of the invention will suggest themselves to those skilled in the art.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. Germicidal agent for use in aqueous systems, which germicidal agent comprises hydrogen peroxide, a corrosion inhibitor and a synergistic amount of a synergistic ingredient of at least one of the following:

(a) a p-hydroxybenzoic acid compound selected the group consisting of p-hydroxybenzoic acid, salts thereof and alkyl esters thereof of from 1 to 4 carbon atoms in the alkyl moiety;

(b) at least one nitrogen heterocyclic aromatic compound which does not decompose upon reaction with H_2O_2 and which contains at least one hydroxyl group or carboxyl group and which may be in salt or alkyl ester form, wherein the alkyl moiety has of from 1 to 4 carbon atoms;

(c) an aminosulfonic acid of the formula R_2NSO_3H wherein R is hydrogen or alkyl of from 1 to 6 carbon atoms, or a salt of such aminosulfonic acid.

2. Germicidal agent as claimed in claim 1 wherein said synergistic ingredient is in the form of an aqueous solution.

3. Germicidal agent as claimed in claim 2 wherein said synergistic ingredient is in the form of an aqueous mineral acid solution.

4. Germicidal agent as claimed in claim 1 wherein acid synergistic ingredient is contained in an amount comprising from 0.1 to 5 weight percent of the total germicidal agent.

5. Germicidal agent as claimed in claim 1 wherein said p-hydroxybenzoic acid compound is p-hydroxybenzoic acid.

6. Germicidal agent claimed in claim 5 wherein said p-hydroxybenzoic acid compound is a salt of p-hydroxybenzoic acid.

7. Germicidal agent as claimed in claim 6 wherein said p-hydroxybenzoic acid compound is an alkyl ester of p-hydroxybenzoic acid.

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8. Germicidal agent as claimed in claim 1 wherein said nitrogen heterocyclic compound contains at least one hydroxyl group.

9. Germicidal agent as claimed in claim ~~9~~ 1 wherein said nitrogen heterocyclic aromatic compound contains at least one carboxyl group.

10. Germicidal agent as claimed in claim 1 wherein said aminosulfonic acid is one wherein R is hydrogen.

11. Germicidal agent as claimed in claim 1 wherein said aminosulfonic acid is one wherein R is alkyl of from 1 to 6 carbon atoms.

12. Germicidal agent as claimed in claim 1 wherein said nitrogen heterocylic aromatic compounds contains only one nitrogen ring atom.

13. Germicidal agent as claimed in claim 1 wherein said nitrogen heterocyclic aromatic compound is hydroxyquinoline.

14. Germicidal agent as claimed in claim 1 wherein said nitrogen heterocyclic aromatic compound is a pyridinedicarboxylic acid.

15. Germicidal agent as claimed in claim 1 wherein said nitrogen heterocyclic aromatic compound is 8-hydroxyquinoline.

16. Germicidal agent as claimed in claim 1 wherein said nitrogen heterocyclic aromatic compound is dipicolinic acid.

17. Germicidal agent as claimed in claim 1 wherein said H_2O_2 is contained in the form of an aqueous solution.

18. Germicidal agent as claimed in claim ~~18~~ 1 wherein said H_2O_2 is contained in the form of an aqueous stabilizer solution.

19. Germicidal agent as claimed in claim 1 containing only component (a).

20. Germicidal agent as claimed in claim 1 containing only component (b).

21. Germicidal agent as claimed in claim 1 containing only component (c).

22. Germicidal agent as claimed in claim 1 containing components (a) and (b).

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23. Germicidal agent as claimed in claim 1 containing components (b) and (c).

24. Germicidal agent as claimed in claim 1 containing components (a) and (c).

25. Germicidal agent as claimed in claim 1 containing components (a), (b) and (c).

26. Method of rendering a liquid medium resistant to germ which method comprises treating said medium with a germicidal effective amount of an agent as claimed in claim 1.

27. Method as claimed in claim 26 wherein said germicidal agent is applied in a concentration of 0.01 to 2 milliliters of a 35% aqueous H_2O_2 solution per liter of the medium being treated.

*

SUBSTITUTE

REMPLACEMENT

SECTION is not Present

Cette Section est Absente